Regression Analysis for the Adsorption Kinetics of Methylene Blue onto Activated Carbon

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ABSTRACT

Adsorption is the preferential partitioning of substances from the gaseous or liquid phase onto the surface of a solid substrate and is an effective technique for removing harmful substances. Dyes are coloured compounds used in industries and pose certain hazards and environmental problems. Dyes can have acute and/or chronic effects on exposed organism. Due to their chemical structure, dyes possess a high potential to resist fading on exposure to light and water. Chemical kinetics explains how fast the rate of reaction occurs and also on the factors affecting the reaction rate, the higher the value of r^2 (regression coefficient) for a pseudo second-order kinetics (close to 1) suggests this model can be used to represent the kinetic uptake of methylene blue onto activated carbon .Kinetic experiments were carried out for the adsorption of methylene blue on activated carbon for different initial concentrations and were fitted to the pseudo first-order and pseudo second-order kinetics. Graphical representations of the pseudo first-order and pseudo second-order kinetics are carried out followed by three error analysis techniques: Least square test, Chi square test and standard deviation. The adsorption process was found to follow pseudo second-order kinetics, least error and high regression coefficient, and was found to be directly proportional to the initial concentration. Hence, determination of the order of the adsorption kinetics can be useful in estimating the time required to remove methylene blue and quantity of activated carbon that is required to remove different initial concentration of methylene blue.

1. ADSORPTION

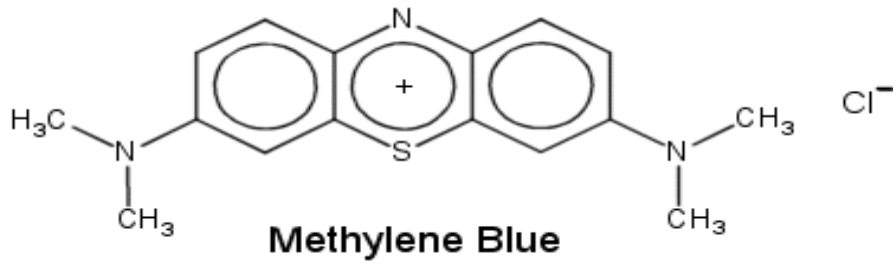
Assimilation of molecular species throughout the bulk of the solid or liquid is called as adsorption. It consists of two components: adsorbate, adsorbent. Adsorbing phase is the adsorbent, and the material concentrated or adsorbed at the surface of that phase is the adsorbate.

Types of adsorption:-

- Physisorption
- Chemisorption
- Exchange Adsorption

2. MATERIAL USED

The dye used in all the experiments was methylene blue. The structure of methylene blue is given by:



Methylene Blue

Amorphous solid consisting of micro-crystallites with a graphite lattice, activated carbon, is usually prepared in small pellets or a powder. Activated carbon can be manufactured from carbonaceous material, including coal, peat, wood, or nutshells. Activated carbon is used for adsorption of organic substances and non-polar adsorbates and it is also usually used for waste gas (and waste water) treatment. Since activated carbon is highly porous, cheap and non-polar, it is used is adsorption of dyes like Methylene Blue

3. REACTION RATES

- **Pseudo first order**

The adsorption of methylene blue following the first order kinetics can be represented as-

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

Where qe- adsorption capacity at equilibrium
q_t - adsorption capacity at time t
k_1- rate constant of pseudo-first order sorption

Upon integration and applying boundary conditions, $q_t = 0$ to $q_t = q_t$ at $t = 0$to $t = t$;

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$$

- **Pseudo second order**

The adsorption of methylene blue following the second order kinetics can be represented as-

$$\frac{dq_t}{dt} = k(q_e - q_t)^2$$

Upon integration and applying boundary conditions, $q_t = 0$ to $q_t = q_t$ at $t = 0$ to $t = t$;

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e} t$$

4. OBSERVATIONS

Co- Initial concentration of methylene Blue

Initially we had values of qt vs t(mins) for different Co values. The value of qe is taken as the last qt value (at t=120 mins). Then the values of Ln(qe-qt) and t/qt for different values of t are found out.

Following are the values obtained for adsorption of Methylene Blue on Activated carbon at different initial concentrations.[1]

Co=100			
t(mins)	**qt**	**ln(qe-qt)**	**t/qt**
2	198	2.484907	0.010101
5	200	2.302585	0.025
10	202	2.079442	0.049505
20	205	1.609438	0.097561
30	206	1.386294	0.145631
60	207	1.098612	0.289855
90	208	0.693147	0.432692
120	210	0	0.571429

Co=150			
t(mins)	**qt**	**ln(qe-qt)**	**t/qt**
2	220	2.995732	0.009091
5	225	2.70805	0.022222
10	230	2.302585	0.043478
20	236	1.386294	0.084746
30	237	1.098612	0.126582
60	238	0.693147	0.252101
90	239	0	0.376569
120	240	0	0.5

Co=150			
t(mins)	**qt**	**ln(qe-qt)**	**t/qt**
2	220	2.995732	0.009091
5	225	2.70805	0.022222
10	230	2.302585	0.043478
20	236	1.386294	0.084746
30	237	1.098612	0.126582
60	238	0.693147	0.252101
90	239	0	0.376569
120	240	0	0.5

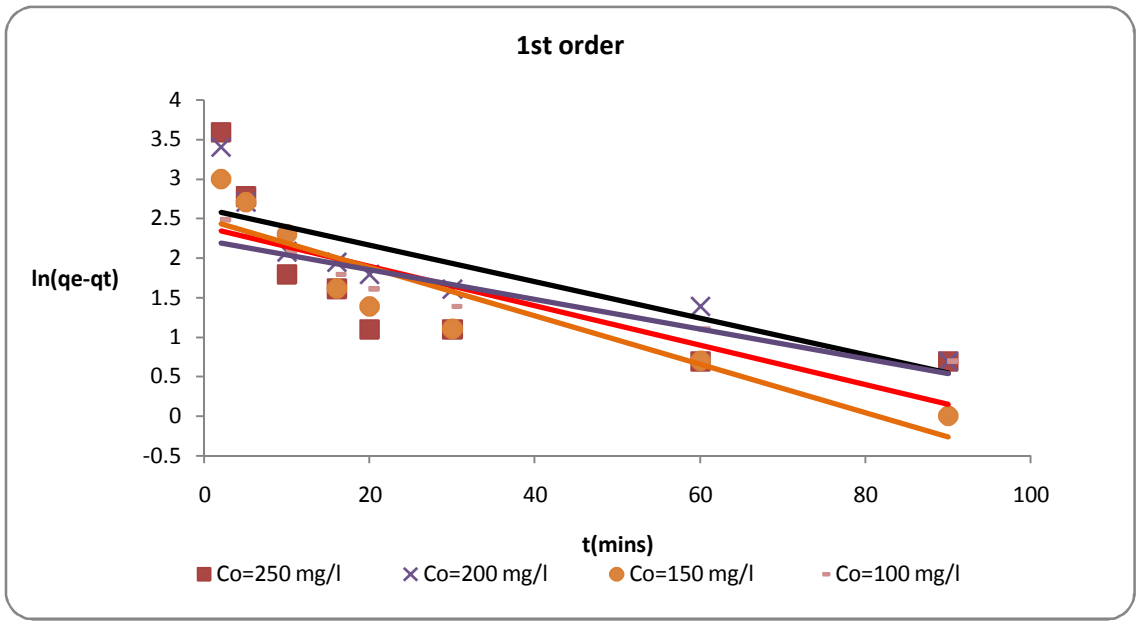
Co=250			
t(mins)	qt	ln(qe-qt)	t/qt
2	290	3.583519	0.006897
5	310	2.772589	0.016129
10	320	1.791759	0.03125
20	323	1.098612	0.06192
30	323	1.098612	0.092879
60	324	0.693147	0.185185
90	324	0.693147	0.277778
120	326	0	0.368098

5. GRAPHICAL REPRESENTATION

Using pseudo first and pseudo second order kinetics equations, line equations for different Co values are formed and plotted. The values of the regression coefficient at different values of t for both pseudo first and pseudo second order kinetics are calculated.

The combined graphs for pseudo first and pseudo second order kinetics are shown below:-

1st Order for all the concentrations



2nd Order for all the concentrations

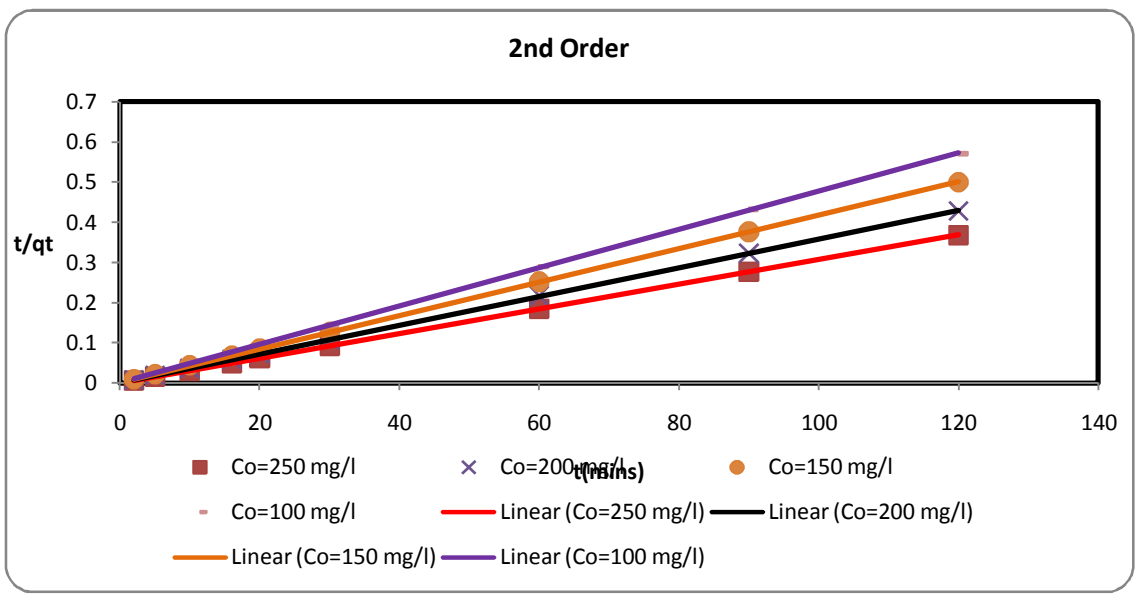


Table 1(Regression coefficient)

Initial Concentration (mg/l)	1st order	2nd order
100	0.8867	0.99999
150	0.8417	1
200	0.7475	1
250	0.5529	1

6. ERROR ANALYSIS

After forming the Line equations for pseudo first and pseudo second order kinetics, three different error analysis techniques: Least square test, Chi square test and standard deviation, were used to calculate the magnitude of error and to predict the order. Following table shows the error analysis details:-

Table 2(Error Analysis)

Initial Concentration (mg/l)	Least Square		Chi Square		Standard Deviation	
	1st order	2nd order	1st order	2nd order	1st order	2nd order
100	0.3	0.01	0.12	10^(-13)	1.499	0.13
150	2.39	0.0007	0.48	10^(-12)	3.67	0.01
200	1.213	0.009	1.196	0.000000009	6.2	0.2
250	3.69	0.0001	2.39	0.0007	9.1	0.04

7. CONCLUSION

- The adsorption of methylene blue onto activated carbon was found to be well represented by the pseudo first-order and pseudo second-order kinetics.[1]
- Chemical kinetics explain how fast the rate of reaction occurs and also on the factors affecting the reaction rate. , the very higher $\mathbf{r^2}$ values for a pseudo second-order kinetics suggests that this model can be used to represent the kinetic uptake of methylene blue onto activated carbon. Refer table 1
- The low $\mathbf{r^2}$ value of pseudo first-order kinetics obtained show that the method fails to well represent the kinetics of methylene blue onto activated carbon.
- The adsorption of methylene blue onto activated carbon was found to follow pseudo second-order kinetics
- Rate of adsorption is directly proportional to the initial concentration which can be depicted by the study at four different concentrations.

- Looking at table 2, we see that second-order kinetics shows very less errors as compared to first order kinetics and hence it can be concluded that adsorption of methylene blue onto activated carbon follows second order kinetics.

8. REFERENCES

[1] K. Vasanth Kumar: *Linear and non-linear regression analysis for the sorption kinetics of methylene blue onto activated carbon.* Journal of Hazardous Materials B137 (2006) 1538–1544

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